

FUNDAMENTALS OF SURFACE CHEMISTRY IN FLOTATION DEINKING

Project F00904

Report 2

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

February 1998

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

FUNDAMENTALS OF SURFACE CHEMISTRY IN FLOTATION DEINKING

Project F00904

Report 2

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

Y. Deng

February 1998

ABSTRACT

This report is concerned with increasing utilization of recycled fiber and, more specifically, with minimizing fiber loss and maximizing deinking efficiency in flotation deinking. The research program was started in May 1995. The results obtained in Fiscal Years 95-96 and 96-97 have been given in Progress Report I (February 1997). Two papers based on this study, "Contact Angle Measurement of Wood Fibers in Surfactant and Polymer Solutions" and "True Flotation and Physical Entrainment: The Mechanisms of Fiber Loss in Flotation Deinking," have been accepted for publication by Wood and Fiber Science and Nordic Pulp and Paper Research Journal, respectively. The current report will focus only on the results completed in the 97-98 FY.

Although flotation deinking is considered to be one of the most effective deinking methods, many physicochemical properties, such as ink removal efficiency, froth structure, fiber loss mechanisms, and filler flotation during flotation deinking, remain unclear. To improve deinking efficiency and reduce fiber loss, the surface chemistry of ink, fiber, filler, air bubble, and other colloid materials in flotation deinking has to be studied.

The objectives of the research program conducted in FY 97-98 are to:

- a. Study the surface chemistry of different collectors in toner flotation deinking.
- b. Study the effect of fiber types on fiber loss.
- c. Study the role of surfactant in the ink-fiber detachment.
- d. Study the effect of old magazine (OMG) on the ink removal of old newsprint (ONP).

The main results obtained in this research program indicate that

- a) Cationic surfactants are the best surfactant systems that have been examined in this study, and these surfactants can be used as both collector and frothing agents for the flotation deinking of xerographic papers.
- b) Both fiber adhesion and physical entrainment will contribute to fiber loss, but the entrainment is the dominating factor.

- c) The addition of OMG will not enhance the ink removal of ONP in flotation deinking. The improvement of ONP brightness in the presence of OMG is solely caused by introducing more fillers and high-quality fibers.
- d) The adsorption of the complex of fatty acid and calcium ions on toner particles will not increase the hydrophobicity of toner particles.
- e) Nonionic surfactant, TX-100, will reduce the hydrophobicity of ink, fibers, fines, and fillers.

Because the objectives studied in 97-98 FY are relatively broad and independent of each other, the results accomplished in 97-98 FY will be divided into four sections:

1. Collect chemistry in flotation deinking of xerographic papers;
2. Fiber loss in flotation deinking: effect of fiber types;
3. The role of surfactant in the ink-fiber detachment;
4. Effect of OMG on the flotation deinking of ONP, and fiber loss mechanisms.

1. COLLECT CHEMISTRY IN FLOTATION DEINKING OF XEROGRAPHIC PAPERS

1.1. Background

The recycling of wastepaper is of growing importance due to the shortage of fiber supply and the restricted government regulations on solid wastepaper landfills. Although the paper recycling rate has increased steadily, the quality and cost of recycled fibers are still incompatible with virgin fibers.

Flotation deinking is one of the most important separation techniques widely used in paper recycling industry. Flotation deinking involves three main processes: detachment of the ink particles from wastepaper fibers, effective adhesion of the ink particles onto air bubble surfaces, and the removal of ink particles with the froth from flotation cells [1-3]. It has been well known that the hydrophobicity and the particle size of ink particles in flotation slurry are two of the most important factors affecting the ink-air bubble interaction. From a surface chemistry point of view, the higher the hydrophobicity of particle surface, the easier it is to remove ink particles from pulp slurry under similar flotation conditions. To improve the hydrophobicity of floated particles, it is very common to apply a collector in the pulp slurry in mineral flotation.

Many collectors have been successfully used in ore flotation, but few of them have been used in flotation deinking. The most common collector used in flotation deinking is fatty acid in the presence of calcium chloride. Many researchers have focused on the understanding of ink removal by adding fatty acid/calcium collector, but the mechanism involved in this system have not been well understood [1,2]. Although the fatty acid/calcium collector has been traditionally used for flotation deinking of old newsprint and old magazines, Dorris and Page [4] recently indicated that fatty acid/calcium collector can also improve the toner removal efficiency during the flotation. They suggested that the increased hydrophobicity of toner particles due to the adsorption of calcium soap of fatty acid onto toner surface is the main reason for toner removal improvement. However, this hypothesis has not been validated by experimental results. Although calcium soap of fatty acid is an effective collector for some grades of wastepapers, the deposition of calcium soap of fatty acid on the

flotation equipment and paper machine is a serious problem. Therefore, it will be beneficial to the paper industry if more effective collectors that do not have negative effects on the papermaking process can be developed.

It was found that the deinking of mixed office paper by flotation is more difficult than other wastepapers because a) toner is usually fused into the pores of papers and strongly adhered to the fiber surfaces, resulting in a poor toner-fiber separation during repulping [5,6], and b) the broad particle size distribution and the disk-like shape of toner particles result in a poor attachment between toner particles and air bubbles [7, 8]. Based on these understandings it is believed that the toner particles must be kept hydrophobic in flotation cell and the optimum particle size must be achieved in order to improve the flotation deinking efficiency of toner printed papers.

This study is to develop a fundamental understanding of collector chemistry in flotation deinking of toner printed papers. The relationship between collector and toner surface hydrophobicity was studied. The agglomeration of toner particles in different collector solutions was examined. Finally, the effects of toner hydrophobicity and toner particle size on the flotation efficiency were investigated.

1.2. Experimental

1.2.1. Chemicals

Triton X-100 (TX-100, a nonionic alkylphenoxy polyethoxy ethanol compound, analyze grade, J. T. Backer Inc.), kerosene (commercial product), sodium oleic acid sodium salt [Aldrich, 98%], dodecyltrimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$, DTMAB, Aldrich, 99%], cetyltrimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$, CTMAB, Aldrich, 95%], and calcium chloride [Aldrich, analytical pure] were used as received.

1.2.2. Contact angle measurements

The surface tension of liquid was measured by a dynamic contact angle analyzer (Cahn DCA 312) using a glass plate. Toner samples for contact angle measurement were made by copying 3 layers of Xerox toner on both sides of a

transparency. The coated transparency was cut into 20mm x 30mm pieces before use. The wetting force of coated toner film in different solutions was measured, and the contact angle was calculated using Wilhelmy principle. Both surface tension and contact angle measurements were repeated several times until a stable reading was obtained.

1.2.3. Particle size measurements

The particle size and size distributions of toner suspension in different solutions were measured by a laser diffraction based particle size analyzer (Malvern 2600, Malvern Instruments, MA). The system consists of 2mW He-Ne Laser (633nm wavelength), a Transmitter with 9mm beam expansion, a Receiver with a Fourier transform lens, and a 31 element solid state detector array in concentric semicircular annuli design. The sample used for particle size analysis were made by dispersing Xerox toner in a pulp filtrate in the presence or absence of surfactant.

1.2.4. Flotation deinking

The pulp was made from bond papers printed by Xerox toner with a fixed pattern of X. The papers were pulped at pH of 9.3 and a consistency of 10.5% without adding any chemicals except sodium hydroxide. A laboratory flotation cell was used to conduct the flotation deinking. The deinking cell was made from a polyacrylate pipe with a height of 80cm and a diameter of 10cm. Nitrogen was blown into the pulp suspension at a rate of 14 ± 0.075 SLPM (standard liter per minute) through an air filter (pore size 50 μm) at the bottom of the flotation cell. The air flow rate was measured by an Omega FMA1700/1800 flowmeter. The consistency of the pulp used in flotation was 0.5%. The flotation time was 10 minutes for all experiments.

The handsheets for brightness analysis were made on a 15-cm Büchner funnel according to TAPPI standard method T218 om-91. The brightness of a handsheet was measured by a UV-VIS spectrophotometer (Shimadzu UV-160A) using TAPPI Standard method T452 om-92.

1.3. Results and Discussion

1.3.1. Calcium soap of fatty acid as a collector in toner flotation deinking

In the flotation deinking of mixed office wastepapers, a nonionic surfactant has been commonly used as a dispersant and frothing agent. However, the addition of a nonionic surfactant, such as TX-100, will reduce the hydrophobicity of toner particles, therefore the toner removal efficiency by flotation will be decreased. The reduction of toner particle hydrophobicity due to adsorbed surfactant can be clearly seen from Fig. 1, i.e. the advancing contact angle of aqueous solution on a toner film decreases as the concentration of TX-100 increases. When the concentration of TX-100 increases from 0 to 80mg/L (the typical concentration for mixed officewaste deinking in industry practice), the advancing contact angle decreases from 140 to 75 degrees. With a further increase in concentration to 200mg/L, the advancing contact angle decreases to 10 degree or even lower. The significant decrease in the contact angle must result in a reduction in deinking efficiency as will be discussed later.

Because nonionic surfactant usually leads to a reduction in the contact angle of toner particles in pulp suspension, it is interesting if there are some collectors that can restore the contact angle of toner particles. It has been known that calcium soap of fatty acid can be used as a collector for both old newsprint and mixed office waster papers [4,9,10]. Therefore, the collector chemistry of calcium soap of fatty acid was first examined in this study.

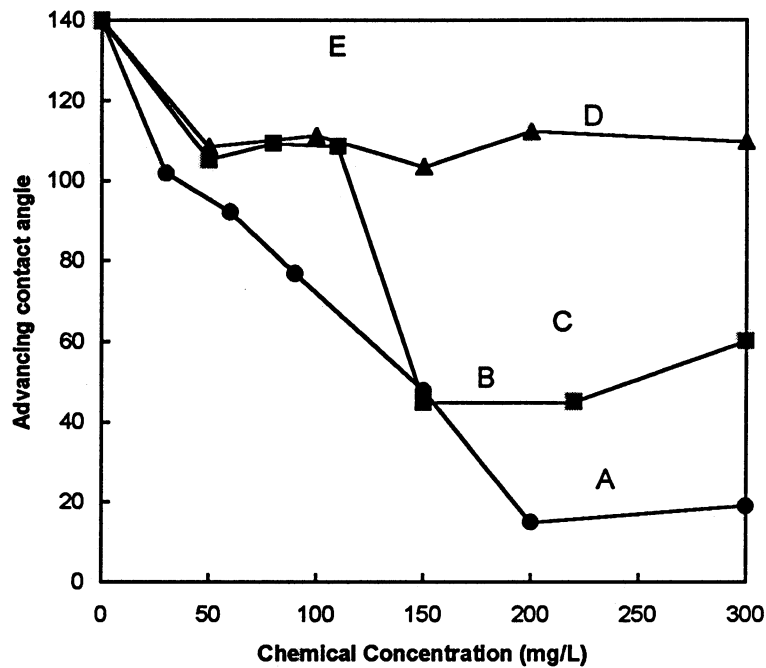


Fig. 1. Advancing contact angle of toner film in aqueous solutions as a function of A: TX-100 concentration without any other chemicals; B: TX-100 concentration in the presence of 50 mg/L sodium oleic acid and 250 mg/L calcium chloride; C: sodium oleic acid concentration in the presence of 500 mg/L calcium chloride.

The contact angle of toner film in water as a function of sodium oleic acid concentration in the presence of 500mg/L calcium chloride is also shown in Fig. 1. It can be seen that as the concentration of sodium oleic acid increases, the advancing contact angle decreases rather than increases. . This suggests that although the complex formed by sodium oleic acid and calcium chloride is hydrophobic, the hydrophobicity of toner surface will not be improved by adsorption of this complex because the hydrophobicity of toner itself is higher than that of calcium soap of fatty acid aggregates.

To effectively remove toner particles from pulp slurry, a relatively stable foam is essential. The common method to generate a foam layer is to add frothing agent directly into pulp suspension during stock preparation. Therefore, it is very interesting to know how the interaction between calcium soap of fatty acid and a frothing agent will affect the hydrophobicity of toner particles in a pulp system. Fig. 1 shows that in the presence of 50 mg/L sodium oleic acid and 250 mg/L calcium chloride, the toner remained at a high contact angle (>105 degrees) until the concentration of TX-100 was increased up to 130 mg/L. Comparing that with the contact angle obtained in the absence of sodium oleic acid/calcium ions (curve A in Fig. 1), it can be seen that calcium soap of fatty acid can protect the toner surface from the reduction of the hydrophobicity due to the adsorption of TX-100. This effect is more significant at low TX-100 concentrations (< 130 mg/L). When TX-100 concentration is higher than 130 mg/L, the advancing contact angle of toner film suddenly decreased from 105 to 45 degrees. Although the reason for this sharp decrease is not clear, the solubilization of fatty acid by TX-100 at the concentration close to its critical micellization concentration (185 mg/L) may be one of the possible effects.

Although the hydrophobicity of ink particles is one of the dominating factors in flotation deinking, the particle size is also critical. Obviously, an effective collector should not only remain a high contact angle of ink particles in solution, but also agglomerate the ink particles into an optimum size. Fig. 2 shows the particle size in aqueous solutions as a function of the concentration of TX-100 or sodium oleic acid. It has been noted from toner particle size measurements that the number distribution of toner particle the presence of TX-100 has normal Gauss distribution, regardless of the concentration of TX-100. It can be seen that, when TX-100 was used alone, the toner particle size slightly decreased as the concentration of TX-100 was increased. This is not surprising because although the toner particles can be dispersed in the pulp filtrate and stabilized by adsorbed anionic trash (they aggregate and floated in pure water), there must be some small toner aggregates because anionic trash in the pulp filtrate is not a very effective stabilizer. When TX-100 was added in the suspension, these small toner aggregates were redispersed by surfactant resulting in a decrease in the average particle size. However, it can also be seen from Fig. 2 that in the presence of 500 mg/L calcium chloride and 20 mg/L TX-100, the particle size of toner suspension increases

as the concentration of sodium oleic acid increases. This suggests that toner particles were aggregated by calcium oleate even in the presence 20 mg/L TX-100. At 90 mg/L of sodium oleic acid solution, the mean toner particle size increased to 27 μm (Sauter Mean Diameter), which was in the optimum size range for flotation reported by Ferguson [2]. It was noted that the increase of collector concentration will not only increase the number average particle size, but also the particle size distribution. For example, it is found that the agglomeration of small particles was more significant than that of large particles.

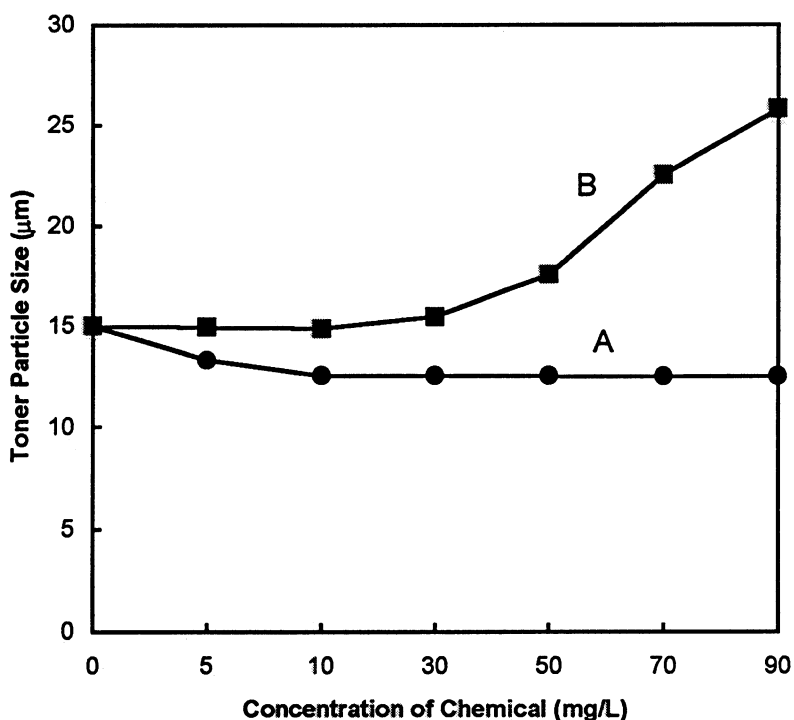


Fig. 2. Toner particle size as a function of A: TX-100 concentration; and B: TX-100 concentration in the presence of 50 mg/L sodium oleic acid and 500 mg/L calcium chloride.

The effect of hydrophobicity and particle size of toner in pulp slurry on the flotation deinking efficiency was investigated by measuring the brightness gain of the handsheets made from deinked xerographic fibers. The brightness gain as a function of TX-100 in either the presence or absence of calcium oleate is shown in Fig. 3. It can be seen that in the absence of calcium oleate, the brightness gain increases as TX-100

concentration increases up to 120 mg/L, then decreases as TX-100 concentration further increases. The initial increase in the brightness at low TX-100 concentration is due to the increase in the foam stability, and the decrease in the brightness at high concentration is due to the decrease in the hydrophobicity of toner particles by adsorbing TX-100 molecules onto the surface, which is consistent with the contact angle measurement shown in Fig. 1. This behavior has also been previously reported [11].

It is reasonable to assume that toner removal can be enhanced by adding a fatty acid and calcium ions because the toners have a high contact angle in the solution, as has been reported previously [4]. Surprisingly, our results shown in Fig. 3 indicate that the presence of 50 mg/L sodium oleic acid and 250 mg/L calcium chloride decreases rather than increases the toner removal in similar pulp systems. Although the mechanism of this reduction in flotation deinking efficiency is not clear, the effect of calcium soap of fatty acid on the foam stability and structure must be accounted. It was observed during the flotation experiments that the foam was much less stable in the presence of calcium soap of fatty acid compared with that using TX-100 alone. Because the bubbles were broken during their rise to the top of the flotation cell, some adhered toner particles returned back to the pulp slurry, which may results in a decrease in the flotation deinking efficiency.

1.3.2. Kerosene as a collector in toner flotation deinking

Hydrocarbon materials that have been widely used in the mineral flotation industry as collectors are getting attention in the paper industry. Snyder and Berg [7] described that some hydrocarbon materials can be used as an agglomeration agent for suspended toner particles. Pelton [12] also found that ink particles are more easily adhered to hydrocarbon oil coated glass beads. Miller et al. [13] found that the toner flotation efficiency can be significantly improved by adding 5% tetrahydrofuran or acetone (based on dry waste) into pulp suspension. In a recent study [14], Oguz indicated that a mixture of kerosene, detergent and borax can significantly improve ink removal. Although these findings are interesting, no fundamental study on the collector chemistry using a mineral oil or hydrocarbon material in flotation deinking has been reported in the literature. In this study, the kerosene was used as a model hydrocarbon collector for toner deinking. The contact angle of toner film in water was measured and

the results are shown in Fig. 4. It can be seen that although the advancing contact angle of toner decreases slightly as kerosene concentration is increased, it is still as high as 130 degree at kerosene concentrations of up to 160 mg/L (small kerosene droplets on the surface of solution will be seen with further increases in concentration). However, when TX-100 was added into toner suspension in the presence of 50 mg/L kerosene, the advancing contact angle was decreased. Although this decrease is significant, by comparing with curve C in Fig. 4, it can be seen that the addition of kerosene can restore some of the loss in toner hydrophobicity that is caused by the adsorption of TX-100.

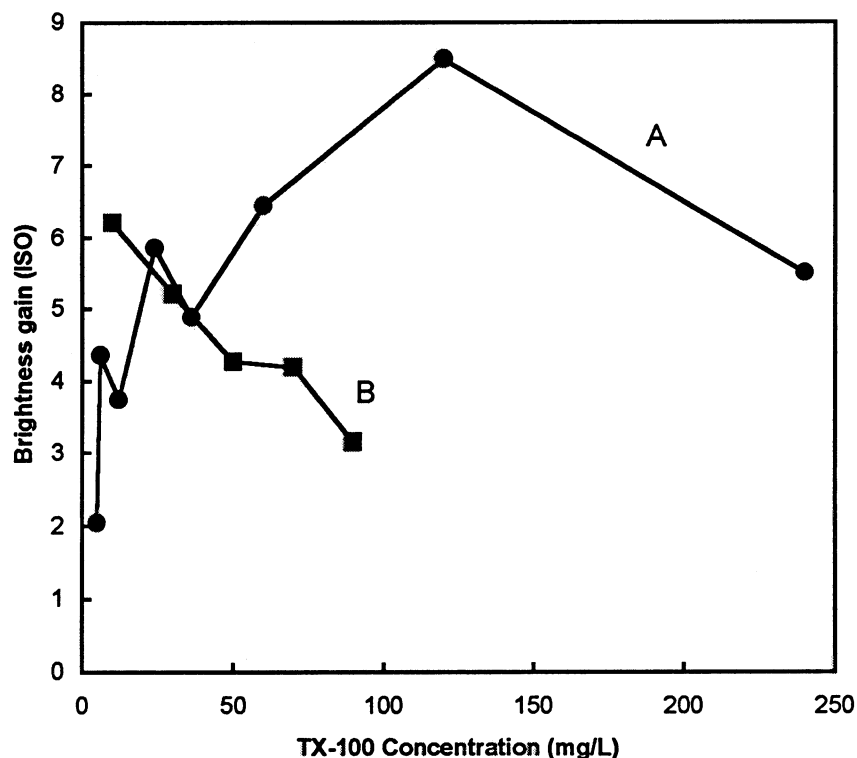


Fig. 3. The brightness gain of handsheed made from deinking fibers as a function of A: TX-100 concentration without other chemicals; B: TX-100 concentration in the presence of 50 mg/L sodium oleic acid and 250 mg/L calcium chloride.

The effect of kerosene on the agglomeration of toner particles in the presence of TX-100 was also examined and the results are shown in Fig. 5. It can be seen that the particle size of toner in the presence of 20 mg/L TX-100 increases significantly as the increase in the kerosene concentration, suggesting a significant agglomeration of toner particles in this solution. It is believed that the agglomeration of toner particles was caused by “oil bridging” mechanism as reported by Berg et al. [7] using other hydrocarbon solvent.

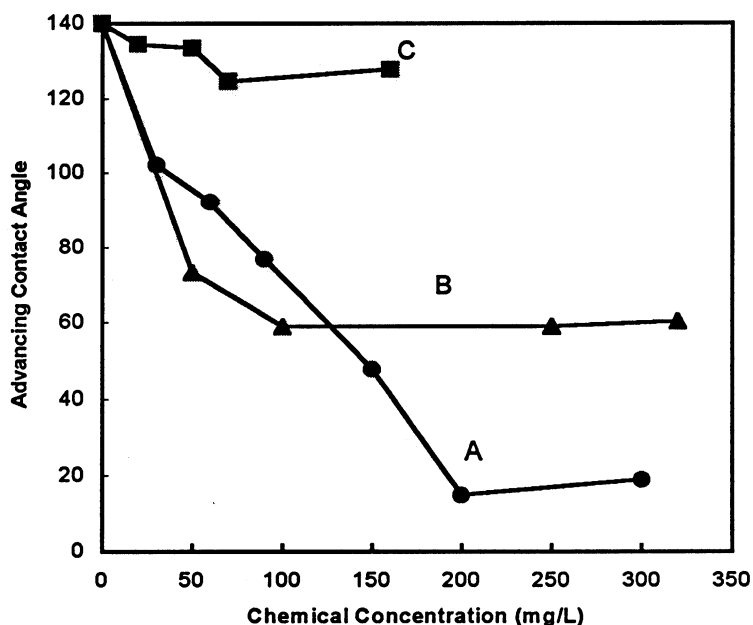


Fig. 4. Advancing contact angle of toner film in aqueous solutions as a function of A: TX-100 concentration without any other chemicals; B: TX-100 concentration in the presence of 50 mg/L kerosene; C: kerosene concentration.

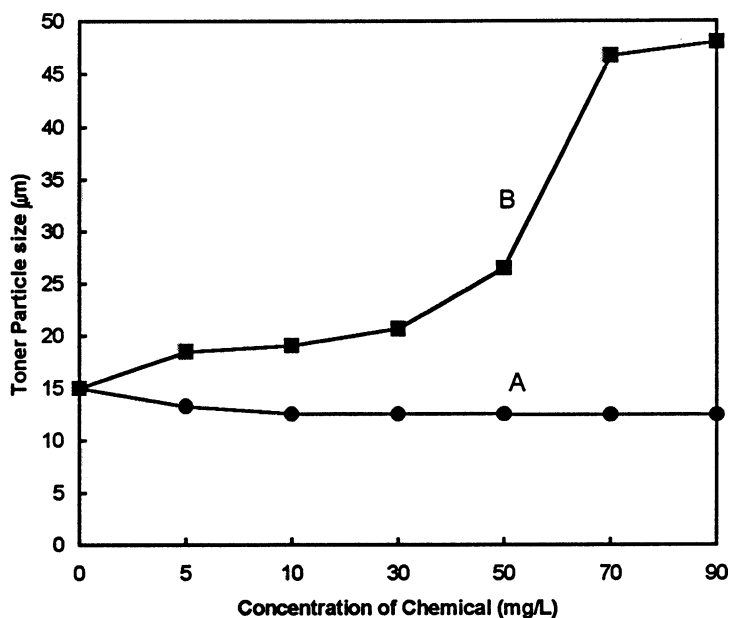


Fig. 5. Toner particle size as a function of A: TX-100 concentration; B: kerosene in the presence of 20 mg/L TX-100.

The effect of kerosene on the flotation deinking efficiency of toner printed papers was studied using TX-100 as a frothing agent. The brightness gain of the handsheets made of recycled fibers is shown in Fig. 6. It can be seen that in the presence of 20 mg/L kerosene, the ink removal is higher than that of without kerosene, particularly at low TX-100 concentration. This is consistent with the contact angle and particle size measurement, i.e., a high contact angle and an optimum particle size result in a high deinking efficiency. The results shown in Fig. 6 indicate that kerosene can be used as a collector for toner flotation deinking when TX-100 is used as a frothing agent.

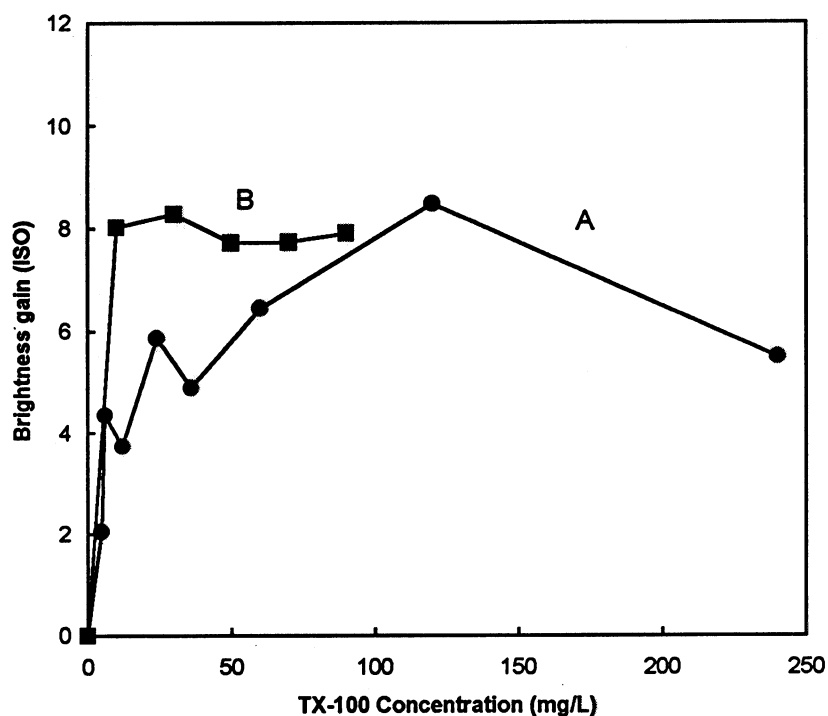


Fig. 6. The brightness gain of handsheet made from deinking fibers as a function of A: TX-100 concentration; B: TX-100 concentration in the presence of 20 mg/L kerosene.

1.3.3. Toner flotation deinking using cationic surfactants

Cationic surfactants have been traditionally used in mineral flotation. One of the advantages of using cationic surfactants is that these chemicals can function as both a collector and a frothing agent for some ores. The effect of cationic surfactant structure on the mineral flotation was studied [15-17]. Although cationic surfactants are very effective for flotation of some mineral particles, limited research [1,2,18,19] has been done using cationic surfactants for flotation deinking. There is no report in the literature on the application of cationic surfactants to deink toner-printed wastepapers.

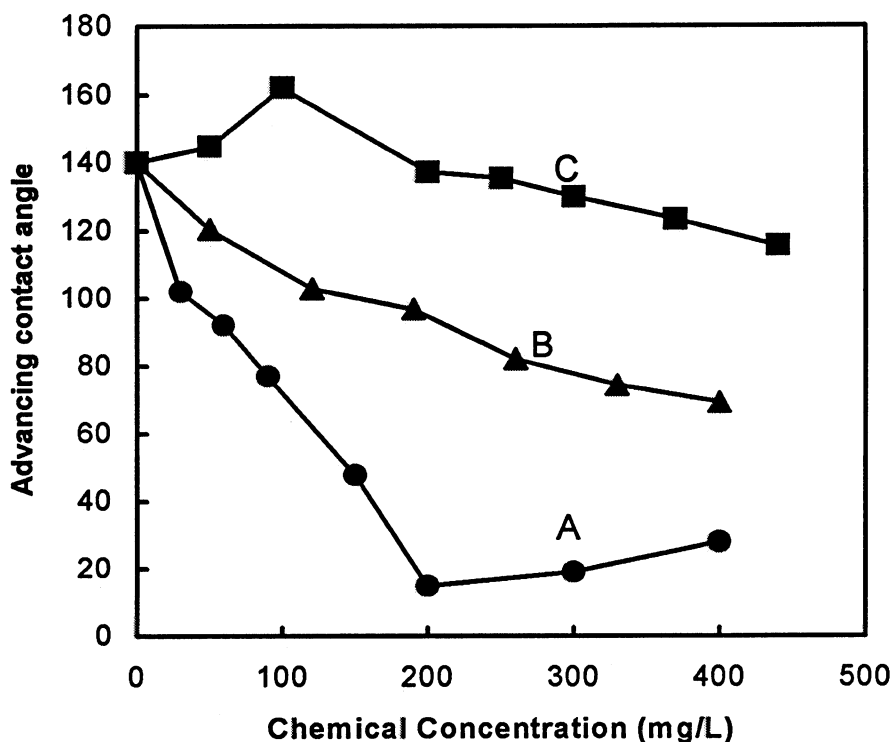


Fig. 7. Advancing contact angle of toner film in aqueous solutions as a function of A: TX-100 concentration; B: DTMAB concentration; C: CTMAB concentration.

Fig. 7 shows the advancing contact angle of toner film in different cationic surfactant solutions. It can be seen that the contact angles of toner film obtained in two different cationic surfactants are much higher than that in the TX-100 solution. More interesting is that the contact angle increases initially as the concentration of CTMAB increases, then decreases as further increase in CTMAB concentration. It is known that the toner particles in wood pulp suspension are negatively charged because of the adsorption of soluble anionic polymers, such as sulphonated lignin and fatty acids from wood fibers, onto the toner surfaces. When cationic surfactant molecules are adsorbed onto these negatively charged toner surfaces, the configuration of adsorbed cationic surfactant should be different from that of anionic and non anionic surfactants. At a low concentration of cationic surfactant, the positively charged surfactant heads anchor to the negatively charged toner surface leaving hydrophobic tail toward the solution. As a result, the contact angle is increased.

However, at a high concentration of cationic surfactant, a double layer adsorption can occur and the hydrophilic heads of cationic surfactant orient to the water phase, which reduced the contact angle. The configurations of cationic surfactant at different concentrations are schematically shown in Fig. 8. It should be noted that no contact angle increase was observed for the cationic surfactant of DTMAB, which may be attributed to the fact that the DTMAB has a shorter hydrocarbon chain than the CTMAB, resulting a more hydrophobic adsorption layer on the toner surface.

The effect of cationic surfactants on the agglomeration of toner particles is shown in Fig. 9. The particle size of toner particles in pulp filtrate was almost a constant when the concentration of DTMAB was increased, but increased steadily with the increase of CTMAB concentration up to 90 mg/L. The particle size increase is consistent with the hydrophobicity increase of toner particles in cationic surfactant solutions. It is believed that in addition to the hydrophobicity effect, the charge neutralization between cationic surfactant and negatively charge adsorbed materials on the toner surface in a pulp filtrate will also affect the toner particle agglomeration.

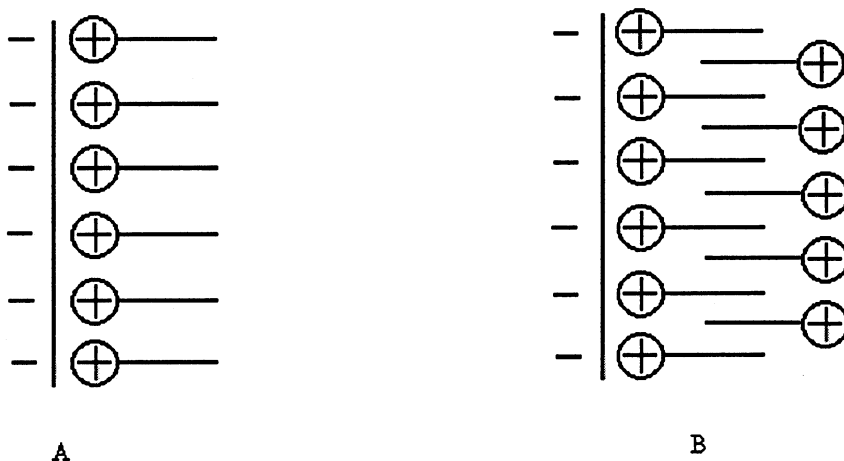


Fig. 8. The orientation of cationic surfactant on a negatively charged toner surface. A: monolayer adsorption at low concentration, and B: double layer adsorption at high concentration.

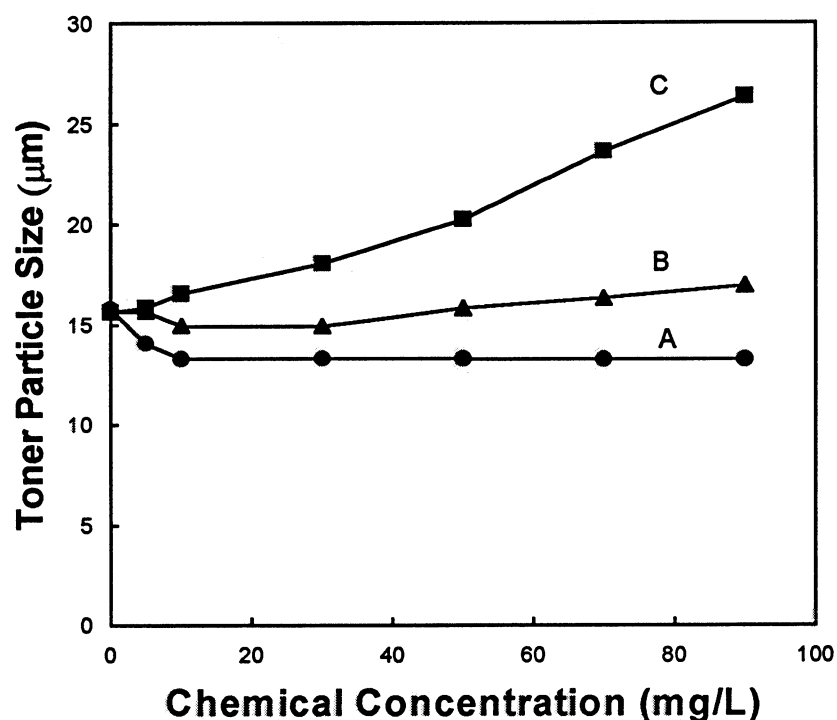


Fig. 9. Toner particle size as a function of A: TX-100 concentration; B: DTMAB concentration; C: CTMAB concentration.

As discussed previously, the toner particle hydrophobicity can remain relatively high and particle size can be increased in CTMAB solutions. It was also found that cationic surfactants are effective frothing agents as well as collectors in pulp suspensions. Therefore, it is not necessary to have a second surface active agent in flotation deinking if a cationic surfactant is used. This advantage may significantly reduce the flotation deinking cost. The brightness gain obtained from handsheets made of deinked fibers as a function of cationic surfactant concentration is shown in **Fig. 10**. It was found that cationic surfactants produced much higher brightness gains than TX-100. The result is consistent with the contact angle and particle size measurements, i.e. CTMAB and DTMAB are very effective collectors and frothing agents for toner flotation deinking.

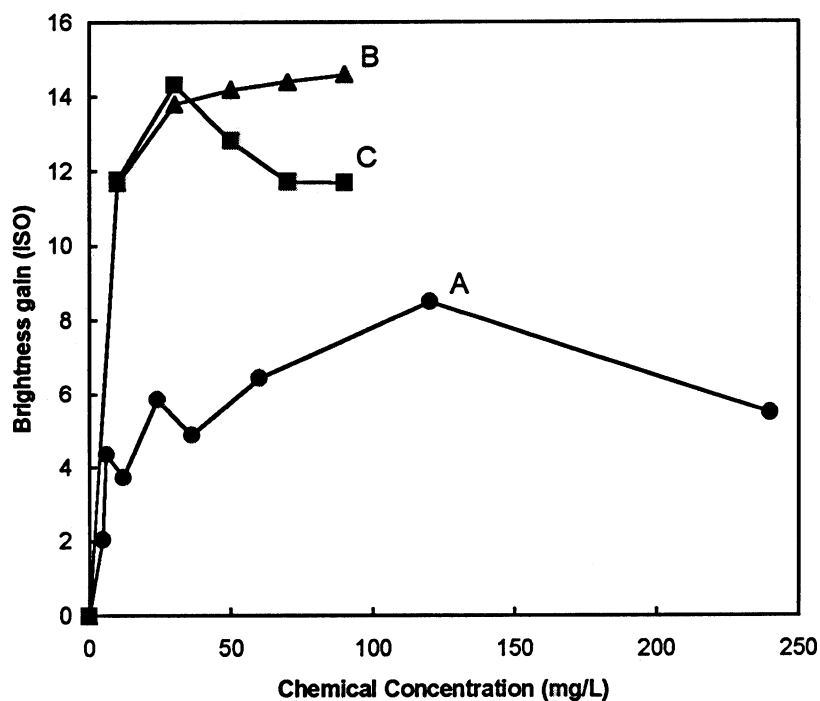


Fig. 10. The brightness gain of handsheed made from deinking fibers as a function of A: TX-100 concentration; B: DTMAB concentration; C: CTMAB concentration.

1.3.4. Concluding remarks

- 1) The contact angle of toner film in water-surfactant solution decreases with the increase of TX-100 concentration regardless if there is a collector. The balance between froth stability and hydrophobicity leads to an optimized concentration for toner removal if TX-100 is used alone.
- 2) The addition of fatty acid/calcium ions causes particle agglomeration but does not increase the contact angle of toner particles. The addition of sodium oleic acid/calcium ions in the flotation process does not enhance the toner removal if TX-100 is used as a frothing agent.
- 3) Kerosene can increase the toner particle size and maintain a relatively high contact angle of toner in TX-100 solution. The flotation deinking efficiency of

toner-printed papers can be improved by adding a small amount of kerosene if TX-100 is used as a frothing agent.

- 4) Cationic surfactant can be used as both a collector and a frothing agent. For the systems investigated in this study, the cationic surfactants provided the best ink removal.

2. FIBER LOSS IN FLOTATION DEINKING: EFFECT OF FIBER TYPES

2.1. Background

Although the deinking efficiency is closely related to the brightness and cleanliness of the fibers, brightness figures without any information on the yield of the deinked fibers have only limited value because the achieved brightness strongly depends on the yield. Low yield caused by high fiber loss is one of the biggest problems in flotation deinking. Reported fiber loss is in the range of 4-24 wt% depending on the processes, equipment, and chemicals used in flotation deinking. For highly sized or waxed fibers, such as old corrugating containers, fiber loss is even higher, and the flotation technique cannot be used for these paper products unless a new technique is established.

Most authors [20-22] have postulated that the fiber loss in flotation deinking is caused by air bubbles routinely adhering to the fibers during the flotation process. In a series of studies on fiber loss in flotation deinking, Turvey [20,21], and Schwinger and Dobias [29] indicated that 1) unprinted fibers do not float; 2) calcium ions can significantly increase fiber loss for printed fibers; 3) nonionic fatty alcohol ethoxylate surfactants cause high fiber loss; and 4) pH plays an insignificant role in fiber loss. From these studies, Turvey [20,21] further concluded that fiber loss is due to the fact that part of the fiber becomes hydrophobic and adheres to air bubbles. However, no direct experimental measurement of fiber surface chemistry can support this assumption. Furthermore, some of the conclusions from Turvey [20] have been argued by other researchers [4,5,22-24] who indicated that unprinted fibers, even very clean bleached fibers, can still float during the flotation deinking process. In contrast to Turvey's study, some recent papers [4,5,24] indicated that the fiber loss in flotation

deinking is solely caused by physical entrainment rather than true flotation. The conflicting experimental results obtained by different researchers suggest that the mechanism of fiber loss in flotation deinking has not been well understood.

It was reported that long fibers float easier than wood fines [22,24]. To explain this phenomenon, Li and Muvundamina [22] assumed that surfactant molecules have different orientations on the fine and fiber surfaces. It is well known that the surface of fines is more hydrophobic than long fibers because of its high lignin content. When surfactants adsorb onto fines, the hydrophobic tails of surfactant molecules anchor onto the hydrophobic sites of fines and leave the charged heads (or hydrophilic parts) toward the water phase. This leads to an increase of hydrophilicity of the surface of wood fines and prevents them from adhering onto air bubble surfaces. For long fibers, on the other hand, the surface is very hydrophilic, and surfactant adsorption is through the interaction between the hydroxyl groups of fiber surfaces and the charged heads of surfactant molecules (or hydrophilic parts of nonionic surfactant), resulting in an increase of hydrophobicity. Li and Muvundamina [22] believed that the increase in hydrophobicity of fiber surfaces was the main reason for fiber removal. Once again, this is only an assumption, and there is no direct experimental measurement to support it.

It is clear that there are many arguments on the fiber loss mechanism. In order to study the effect of fiber surface chemistry on the fiber loss, both unsized and AKD-sized fibers from the same bleached softwood kraft pulp were used in this study. The average fiber length was 2.83 mm. Because the sized fibers have the same geometric property as unsized fibers but totally different of surface chemistry, the contribution of fiber surface chemistry and fiber length to the total fiber loss can be separately studied.

The flotation cell used in this study includes a polyacrylate column (12 cm in diameter; variable in height) and a gas inlet filter. Nitrogen was injected from the bottom of the flotation cell through an air inlet filter. Two types of inlet filters with pore sizes of 10 or 2 μ m were used. Both the fibers that were removed from the cell (fiber loss) and those that remained in the cell were filtered, oven dried, and weighed. The detail description of flotation facility and experiments have been given in our last year's progress report [25]. In our study, the water loss was controlled by varying the froth

height (adding extra columns to the top of the flotation cell) at a fixed nitrogen flow rate and flotation time. This method is totally different from previously reported studies [3,4,24] in which the water loss was controlled by varying the flotation time at fixed froth height. We believe that our method is more scientific for fiber loss mechanism study than the method used in previous studies. The detail discussion can be found in our recently published paper [24].

In the Progress Report of FY96-97 [25] we studied the mechanisms of fiber loss using a AKD-sized and a clean BSK (bleached softwood kraft) pulps. In this progress report, the effects of fiber and surfactant types on the total yield are discussed.

2.2. Experimental

The pulp properties used in this study are given in Table I. *Atlanta Journal-Constitution* and New York Times were used as old newsprint (ONP). The average aging time of ONP used in this study is about 1.5 months. Pump Magazine and Paper Maker Magazine were used as old magazine (OMG). Old magazines were collected different times.

Table I. Fiber properties.

Fiber*	Ash Content (%)	advancing contact angle in water (degree)	Advancing contact angle in 100 g/L TX-100 (degree)	Fiber length (mm)
ONP (<i>Atlanta Journal-Constitution</i>)	0.93%	52	26	1.60
Bond paper	16.24%	28	-	1.79
OMG		-	-	
BSK	0	32	4	2.83
0.2% AKD emulsion sized BSK	0	76	28	2.83
0.6% AKD emulsion sized BSK	0	106	34	2.83

*: ONP: Old newsprint; OMG: Old magazine; BSK: Bleached softwood kraft fiber.

The fiber lengths were determined by image analysis. The width and lumen diameter of fibers were measured using 400× magnification with the aid of OPTIMAS image analysis software. The fiber perimeter was calculated from number average fiber width and lumen diameter. The ash content was obtained at 550 °C according to the TAPPI standard method (T211 om-93).

The PCC content was analyzed by potential titration using EDTA salt as titrate. The pulp slurry was firstly adjusted to pH <3 by adding HCl and stood up for ~0.5 hr. After calcium carbonate dissolved and CO₂ evaporated, ~1 ml NH₃H₂O was added in the solution to bring pH up to ~9.2. The Ca²⁺ concentration was determined by titration using a 0.002M EDTA (ethylenediamine tetraacetic acid disodium, Aldrich, 99+%) solution. A calcium selective electrode (Fisher product) and a glass pH reference electrode (Fisher product) were used as the detector. A detail description about the titration technique can be found from Fisher's product menu.

The sized fibers were made by the reaction of fibers with varying amounts of a cationic AKD (alkyl ketene dimmer) sizing emulsion (Hercon 70, Hercules Inc.) in ~3% fiber consistency for 5 min. The furnishes were filtered and air dried about 2 hr. The air-dried fibers were heated to 100°C in a vacuum oven for ~30 min.

The handsheets for brightness analysis were made on a 15-cm Büchner funnel using TAPPI standard method (T452 om-92). The brightness of the handsheets was measured using a Shimadzu UV-VIS Spectrophotometer (UV-160A).

2.3. Effect of Fiber Hydrophobicity on the Fiber Loss

The flotation of solid materials can be divided into “true flotation” and “entrainment.” True flotation occurs when solids attach to air bubbles and are floated with them. A basic requirement for true flotation is that the solid particles must be hydrophobic enough so that they can strongly adhere onto the bubble surface. Entrainment occurs when particles enter the froth with the water and occupy the spaces between the bubbles. When froth raises up, part of the water and particles entrained in the froth will drain back to the pulp suspension, but the remainders are carried upwards and scraped off. As a result, fiber removal by physical entrainment should be a function of water removal, and at ideal conditions, a linear relationship between fiber removal and water removal is expected. The contributions of true flotation and entrainment in mineral flotation have been discussed, and the following equation has been suggested [26]:

$$R = A + CV_{\text{water}} \quad (1)$$

where R is the total recovery of the given solid suspension at experimental conditions; A is the recovery of the solid by true flotation; C is the concentration of entrained solids in removed water; and V_{water} is the volume of removed water. At ideal conditions, the true flotation A and the concentration C of entrained solids in removed water can be obtained from the intercept and the slope of removed solids versus removed water, respectively.

In order to separately study the true flotation and entrainment of fibers in flotation deinking, a bleached softwood kraft pulp was first used in this study. Direct measurement of wettability using a separated fiber group technique indicated that the receding and advancing contact angles of the bleached softwood fiber in a 100-mg/L TX-100 solution are zero and <5 degrees, respectively. This suggests that the bleached softwood kraft fibers are very hydrophilic and they cannot adhere to air bubbles by hydrophobic force in the flotation process. In other words, the loss of these hydrophilic fibers in the flotation cell should be caused solely by the physical entrainment.

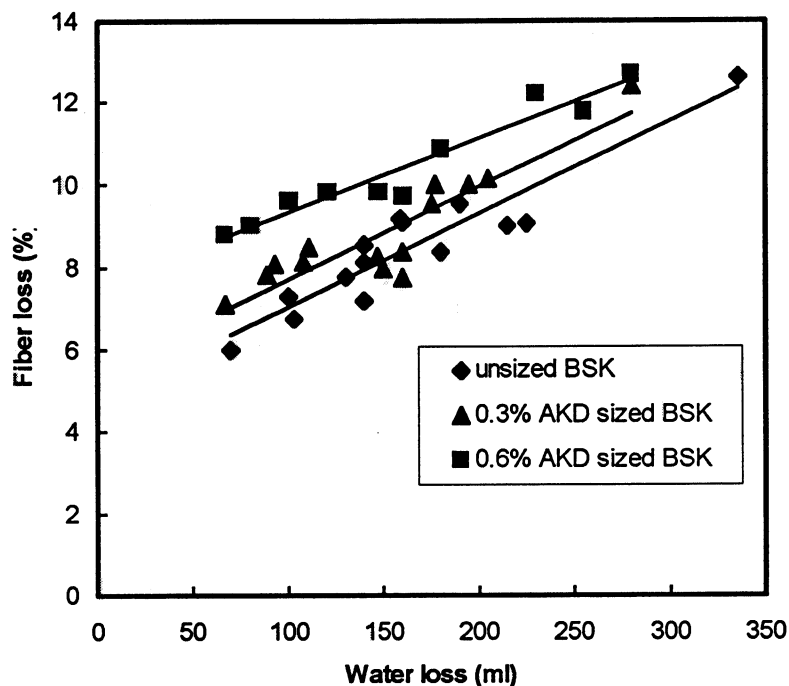


Fig. 11. Fiber loss as a function of water loss for unsized and AKD-sized bleached softwood fibers. The water and fiber losses were measured at different froth heights. Pore size of air inlet filter: 10 μm ; fiber consistency: 0.52%; concentration of TX-100: 100 mg/L; nitrogen flow rate: 1800 cm^3/min ; flotation time: 2 minutes.

Fig. 11 shows fiber loss as a function of water loss for different fibers after a 2-minute flotation. According to **Equation (1)**, a zero intercept of fiber loss against water loss should be expected for these hydrophilic unsized fibers because these fibers have a zero receding contact angle and very low advancing contact angle (<5 degrees). In other words, all floated fibers in this system should be solely caused by physical entrainment. However, the results of **Fig. 11** clearly show that both the slope and intercept for bleached softwood kraft fibers (unsized) are not zero. This strongly indicates that although **Equation (1)** has been used for the mineral flotation system, it cannot be directly used to describe the fiber loss in flotation deinking. It should be noted that **Equation (1)** is based on the assumption that the concentration of entrained (excluding adhered) solids in the froth phase is a constant during the water drainage, and all entrained solid particles will be washed back to the pulp phase if the water is

fully drained from the froth. This may be true if the size of entrained particles is small and the density of the particles is high, such as mineral particles, but it is not the case for wood fibers because some entrained fibers cannot pass through the microchannels between bubbles during the drainage of water in the froth phase due to their large size and small density. As a result, a nonzero intercept of fiber loss plotting water loss must be obtained even though the flotation of wood fibers is solely caused by entrainment. Because some of entrained fibers cannot be washed away during water drainage, a correction for these “unwashable” entrapped fibers must be made in order to use **Equation (1)** for wood fibers. It should be noted that unwashable entrapped fibers are different from true flotation fibers, although both of them cannot be washed away during water drainage. Obviously, the consistency of these “unwashable” entrapped fibers in the froth should be a function of foam structure, fluid dynamics of water in the froth microchannels, the fiber length, and orientation, etc. If all experimental conditions remain constant during the foam raising up in the flotation cell, it can be approximately assumed that the weight of unwashable entrained fibers is constant in the froth. Therefore, **Equation (1)** should be modified to

$$R = A + B + CV_{\text{water}} \quad (2)$$

where B is the weight of unwashable entrained fibers.

Equation (2) indicates that the intercept of the plot of total fiber loss R versus water removal should equal the sum of the fiber loss caused by true flotation A and unwashable entrapped fiber B rather than true flotation A alone, and this intercept is independent of total removed water V_{water} at a fixed flotation time. **Equation (2)** also indicates that although the true flotation A is zero for hydrophilic wood fibers, the intercept of the plot of total fiber loss versus water loss should equal B rather than zero. By plotting total fiber loss against water removal for unsized fibers shown in **Fig. 11**, the weight of “unwashable” entrapped fiber B and the consistency of “washable” entrained fiber C were 0.29 g and 0.8 g/L, respectively.

Fig. 11 also gives the comparison of fiber losses for unsized and AKD-sized fibers. It has been known from our previous study [25] that the advancing contact angles for 0.2 and 0.6% AKD-sized fibers in a 100mg/L TX-100 surfactant solution are

28 and 39 degrees, respectively, which are much higher than that of unsized fibers (<5 degrees) in the same solution. From Fig. 11 it can be seen that the fiber losses of sized fibers are consistently higher than unsized fibers. This result indicates that the fiber surface chemistry will also contribute to the fiber loss. Because both the sized and unsized fibers used in this study have the same length, it is reasonable to assume that the entrainment factors *B* and *C* in Equation (2) are the same for all of the sized and unsized fibers. Therefore, the difference in the fiber loss between unsized and sized fibers is attributed solely to the true flotation *A*. Although this assumption may be too simple, the experimental results of Fig. 11 indicate that the slope *C* is almost constant for all three fibers.

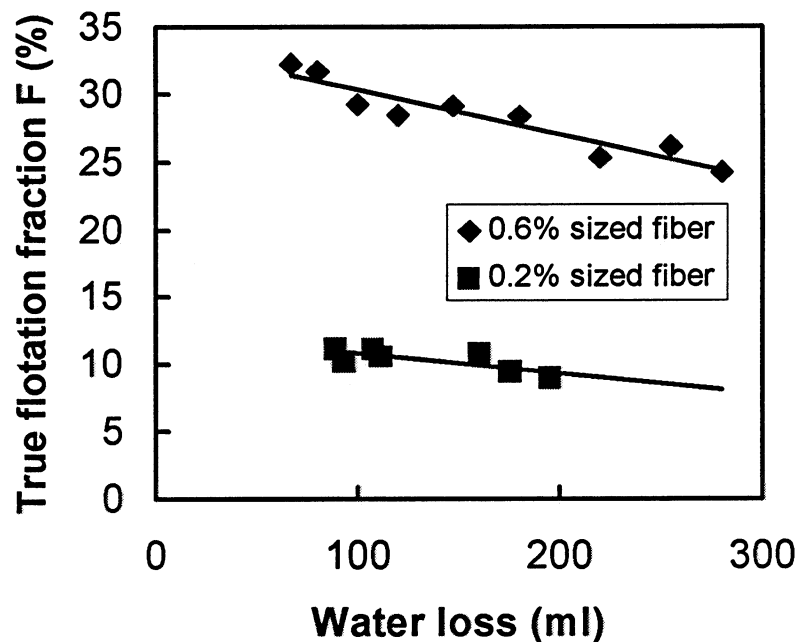


Fig. 12. True flotation fraction *F* as a function of water loss. The true flotation fraction for unsized bleached softwood fiber is assumed as zero. Pore size of air inlet filter: 10 μm ; fiber consistency: 0.52%; concentration of TX-100: 100 mg/L; nitrogen flow rate: 1800 cm^3/min ; flotation time: 2 minutes.

In terms of the above assumption, by applying $B = 0.29$ g and $C = 0.8$ g/L to Equation (2), the weights of true flotation A for 0.2 and 0.6% AKD-sized fibers were obtained and they were 0.025 and 0.15 g, respectively. Comparing the value of true flotation A with total entrained fibers $B + CV_{\text{water}}$, it can be found that true flotation A is smaller than total entrained fibers even for highly sized fibers.

The true flotation fraction F is defined as

$$F = A/R \quad (3)$$

The plots of F as a function of water loss fiber loss are shown in Fig. 12. It can be seen from Fig. 12 that the true flotation fraction F for 0.2 and 0.6% AKD-sized fibers is in the range of 8-12 and 25-33%, respectively, depending on the froth heights. The results suggest that although true flotation is one of the mechanisms of fiber loss, most lost fibers (>88% for 0.2% AKD-sized and >33% for 0.6% AKD-sized fibers) in flotation deinking are mainly attributed to physical entrainment for these systems. Fig. 12 also shows that the true flotation factor F increases as the froth height is increased. This is because the total fiber loss R is decreased, but the true flotation contribution A remains constant when froth height is increased.

Although water loss in flotation deinking has not been considered as a problem in the paper mill, the energy saved by reducing water loss can also benefit the paper industry. Even for a fully closed flotation deinking mill, water loss by froth removal can still be as high as 10% of the total water in the flotation cell, which corresponds to a water loss of ~10 tons/(ton pulp). Because the discharged water contains many deinking chemicals, such as the surfactant and basic materials, reducing water removal is also important for a deinking mill. The results of a study conducted at IPST indicates that properly controlling the froth height and froth stability is a cost-effective method to reduce both water consumption and fiber loss.

2.4. Effect of Fiber Types on Fiber Loss

Fig. 13 shows fiber loss as a function of water loss obtained from different froth heights. The experimental conditions for all of the experiments are the same except different fibers were used.

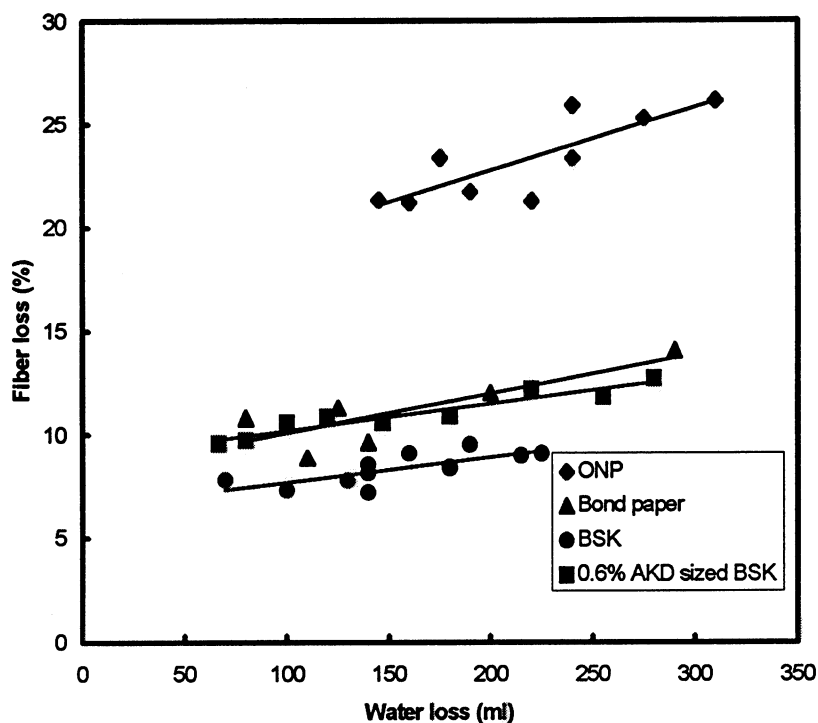


Fig. 13. Fiber loss as a function of water loss for different fibers. Fiber consistency: 0.52%; Surfactant: 100 mg/L TX-100; Nitrogen flow rate: 1800 cm³/min; flotation time: 2 minutes.

It can be seen that, at the same water loss volume (same froth height), the ONP gave the highest fiber loss. The single fiber wettability measurement indicates (see Table I) that the advancing contact angle of ONP in water is 52.2°, that is much higher than bond paper (28.3°) and unsized BSK (32.0°) fibers. Even in 100 mg/L TX-100 solution (the same concentration as used in flotation deinking), the advancing contact angle of ONP fibers is still higher than others. Because of this high contact angle, it is expected that ONP should give a higher fiber loss than bond paper and BSK fibers, which was confirmed by the experimental results shown in Fig. 13. However, it is surprising that ONP gave a higher fiber loss than AKD-sized BSK fibers because 0.6% AKD-sized fiber has a much higher advancing contact angle than ONP in both pure water and 100 mg/L TX-100 solution (see Table 1). This suggests that the higher fiber loss of ONP than other fibers cannot be simply explained by hydrophobicity alone. As discussed in last year's report [25] and our recent publication [23], the physical

entrainment rather than true flotation is the major contributor to fiber loss. Because the physical entrainment strongly depends on the geometry of the fibers and froth structure, the difference in fiber length among these fibers has to be considered. It can be seen from Table I that the fiber length of ONP is much shorter than that of BSK. The higher fiber loss of ONP than AKD-sized fibers may suggest that ONP can be entrapped in the foam network much easier than long BSK fibers. However, more work is needed for a full understanding of the relationship among fiber geometry, foam structure, and fiber loss. It is expected that there may be an optimized fiber length that will cause the highest fiber loss under a fixed foam structure.

2.5. Effect of Different Surfactants On Fiber Loss

Because many different surfactants, including anionic, cationic, and nonionic, have been used in flotation deinking, it is necessary to know if the above conclusion obtained from TX-100 can be applied to other surfactant systems. For this purpose, fiber loss in an anionic surfactant (SDS) and a cationic surfactant (CTMAB) solution was studied. However, it was found that the maximum froth height generated by SDS was only about 20 cm, which did not allow us to study the effect of froth height on fiber loss. Therefore, only cationic surfactant CTMAB was studied in detail. Fig. 14 shows fiber loss as a function of water loss in a CTMAB solution. Although the foam stability and microstructure could be significantly different when different surfactants were used, a similar trend of fiber loss against water loss was observed for the systems of TX-100 and CTMAB, i.e., sized fibers resulted in a higher fiber loss, and the intercept of fiber loss as a function of water loss was not zero. This may suggest that although the true flotation and the physical entrainment will contribute to total fiber loss, the ratio between these two may be different when different surfactants are used.

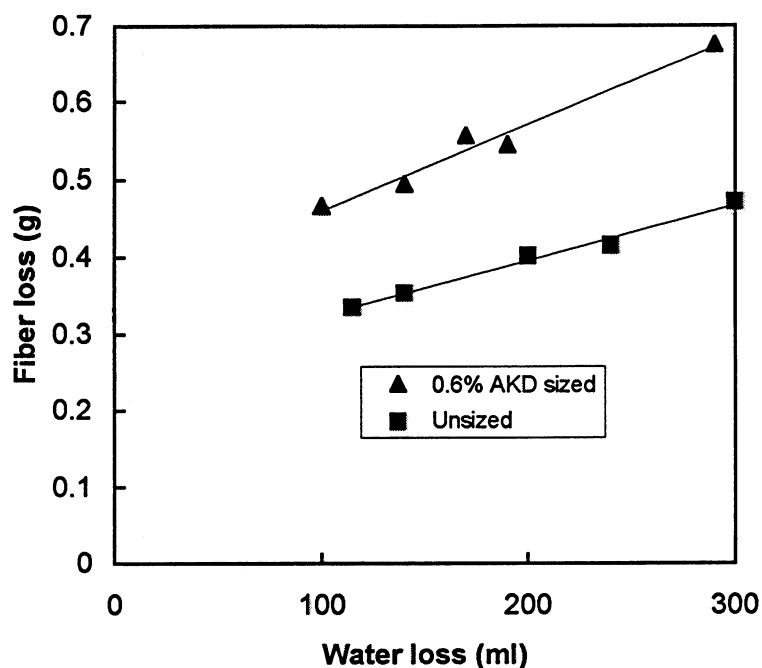


Fig. 14. Fiber loss as a function of water loss for unsized and AKD-sized bleached softwood fibers using cationic surfactant. The water and fiber losses were measured at different froth heights. Pore size of air inlet filter: 10 μm ; fiber consistency: 0.52%; concentration of CTMAB: 100 mg/L; nitrogen flow rate: 1800 cm^3/min ; flotation time: 2 minutes.

2.6. Concluding Remarks

- 1) Both physical entrainment and true flotation will contribute to total fiber loss in flotation deinking, but the physical entrainment is the dominant factor.
- 2) Old newsprint gives a higher fiber loss compared with other fibers when TX-100 was used as a surfactant. Possible reasons for this higher fiber loss may be due to the short fiber length and high hydrophobicity of ONP.

3. THE ROLE OF SURFACTANT IN THE INK-FIBER DETACHMENT

3.1. Background

It is quite common in the deinking operation to add a surfactant in pulps before or during the pulping because most people believe that surfactant can stabilize the ink particles and improve the ink-fiber detachment. However, it is well-known that the adsorption of dispersant has many negative effects, such as rendering the ink particles from hydrophilic to hydrophobic, reducing the agglomeration of ink particles, and increasing the stearic or electrical repulsion force between ink particles and air bubbles. To overcome some of the problems given above, chemicals called displectors have been developed [27,28]. However, the mechanism of dispersant-collector has not been fully understood, and the effectiveness of this chemical has not been widely tested.

The process surfactant used in deinking has many negative effects. One of the problems is that the process surfactant will cause foaming problem in pulpers, which will reduce the capacity of the equipment. Foaming can also cause overflow of the process unit. Although the foaming problem can be partially solved by adding a defoamer agent, it is always cheaper to use less surfactant than to add defoamer. The remaining surfactant in recycled pulp will also cause foaming problems on a paper machine. Another problem related to the remaining deinking surfactants is that they will contaminate recycled fibers, therefore, the fiber-fiber bonding and paper quality will be reduced. The pollution of processing surfactant will also be a serious problem for paper mills. As discussed above, the reduction of the surfactant consumption in the deinking process will improve the paper quality and papermaking process, and reduce the cost of water clarification.

In order to reduce the surfactant consumption, it is important to first understand the real role of surfactant in different deinking steps, including pulping, washing, screening, and flotation. It is interesting to know a) how the surfactant will affect the ink detachment? b) what type of wastepaper needs a dispersant during pulping? c) what type of dispersant is the most effective for certain paper grades? and d) what addition point is most effective and gives the least negative effects? This study will focus on the

role of surfactant in the repulping process, i.e., how the surfactant will affect the ink-fiber detachment.

Calcium soaps of fatty acids are the classic collector used in flotation deinking. Borchardt indicated that calcium ions should be added to the pulp simultaneously or before the fatty acid [29]. The reason for that is because the fatty acid will serve as a dispersant to reduce the particle surface hydrophobicity and particle size. However, it should be argued that if the fatty acids have formed complexes with calcium ions before or during the pulping, the ink detachment will also be reduced. In other words, it may be more effective if this surfactant is added during flotation rather than repulping. Even for nonionic surfactants that are traditionally added into the pulper, any differences between adding surfactant before and after pulping are not very clear. Therefore, it is interesting to know where is the best addition point for flotation deinking surfactant.

3.2. Experimental

The effect of surfactant on the ink-fiber detachment was studied by comparison of handsheet brightness. The recycled fibers from either washing or flotation were used to make a handsheet. Two types of wastepapers were repulped at neutral pH in the presence or absence of surface activities. For the washing experiment, repulped pulps were washed by tap water (~4 times of the volume of pulp slurry) using a dynamic drainage jar equipped with a 125-mesh screen. It is assumed that all of the detached ink in the pulp slurry can be washed away, but the bound ink will still remain in the fiber suspension after washing. By comparing the brightness of the washed fibers that were repulped in the presence of different amounts of surfactant, the role of surfactant in the ink-fiber detachment will be evaluated.

A column flotation cell was used in flotation deinking. The initial distance from pulp suspension to the top of the flotation cell was 5 cm. The wastepaper used for this study included *Atlanta Journal-Constitution* and bond papers. Nonionic surfactant (TX-100) and anionic surfactant (sodium oleic acid) were used.

It was found that the ink particles printed on the ONP are very small, and they can pass through the fiber web and screen easily during the handsheet preparation,

resulting in an increase in the brightness and causing two-sidedness problems on the handsheet. To solve these problems, several retention aids were used during the handsheet preparation. It was found that polyethylene oxide (PEO)/phenol formaldehyde resin (PFR) is the best retention system for ink retention during handsheet preparation. The brightness showed in this study was obtained in the presence of 4 ppm PEO ($M_w = 8$ million, Aldrich) and 8 ppm water-soluble PFR (Cascophen C27, Borden Chemical, Canada) except additional description being given.

3.3. Results and Discussions

3.3.1. The effect of sodium oleic acid on the ink-fiber detachment and ink removal

The brightness of flotation recycled ONP as a function of sodium oleic acid concentration in the presence of 500 ppm CaCl_2 is shown in Fig. 15. The two curves showed in Fig. 15 were obtained in similar flotation conditions but different addition sequences of fatty acid, i.e., in one case, the sodium was added before pulping, and in another case, the sodium surfactant was directly added into the flotation cell. It can be seen that the two processes resulted in only a small difference in handsheet brightness. This suggests that although adding fatty acid before pulping (without Ca^{2+}) may enhance the ink detachment of offset ink from ONP fibers, this enhancement is not significant. This conclusion was further confirmed by washing experiments. In these experiments, the ONP was repulped in the presence of different concentrations of sodium oleic acid. After repulping, the fibers were extensively washed by tap water using a dynamic drainage jar. The brightness of washed fibers as a function of sodium oleic acid concentration is shown in Fig. 16. Two conclusions can be drawn from Fig. 16, 1) the brightness of the handsheet increases as sodium oleic acid concentration is increased regardless of whether the sodium oleic acid was added before or after pulping. This is not surprising because sodium oleic acid will act as a stabilizer for small offset ink particles, which makes ink particles easier to separate from the fiber surface; 2) the addition order of fatty acid will slightly improve the brightness. This is consistent with the flotation deinking results showed in Fig. 15, i.e., adding fatty acid into the pulper will slightly improve the ink detachment from the ONP fiber surface.

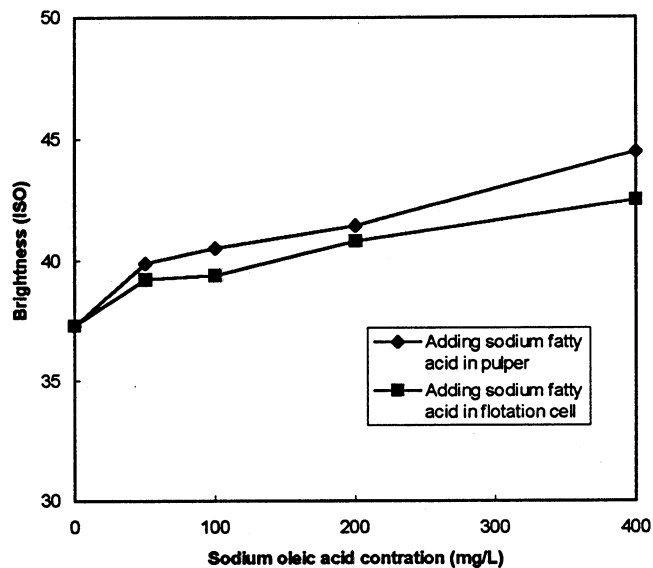


Fig. 15: Brightness of handsheet prepared from flotation deinked ONP. Pulp consistency: 0.52%; Nitrogen flow rate: 1800 cm³/min; Calcium chloride concentration: 500 mg/L (added to the pulp after pulping); Flotation time: 2 minutes.

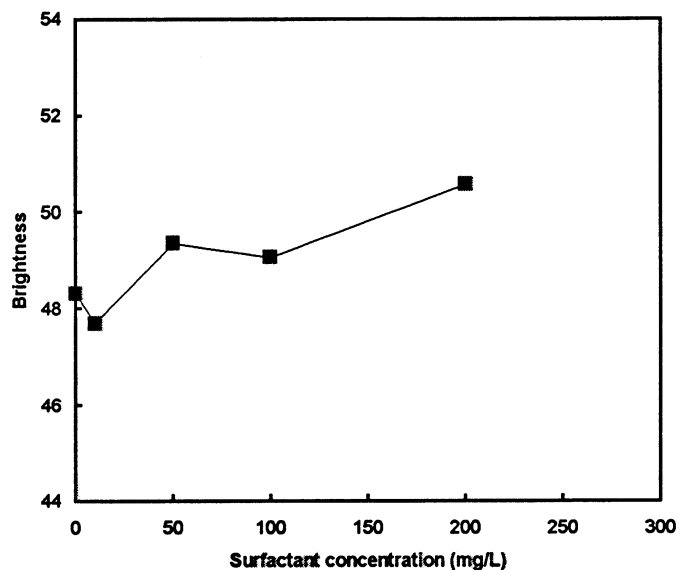


Fig. 16. Brightness of handsheet made from washed ONP. The wastepaper was pulped at a consistency of 1.31% for 30 minutes.

3.3.2. The effect of TX-100 on the ink-fiber detachment and ink removal

The effect of the addition point of nonionic surfactant, TX-100, on the ink removal was studied only by flotation deinking, and the results are shown in Fig. 17. It can be seen from Fig. 17 that TX-100 did not improve ink removal when it was added before pulping, but it did enhance ink removal if it was added after pulping. This is surprising because it is well-known that TX-100 is an effective surfactant for stabilizing many solid suspensions in water. In other words, it is expected that the addition of a stabilizer will enhance the detachment of ink particles from the fiber surface, therefore, improving flotation deinking efficiency. One possible reason for the decrease in the ink removal efficiency may be due to the fact that TX-100 will reduce the agglomeration of ink particles if TX-100 is added before pulping. If this is true, the decrease in the agglomeration of ink particles will result in a decrease particle size; therefore, the ink removal efficiency in the flotation process will be decreased. In contrast to the flotation results, the brightness of handsheets made from washed ONP was increased with the increase of TX-100 concentration when TX-100 was added into the pulp before pulping. This can be seen from Fig. 18. The results obtained from washed ONP suggest that TX-100 will enhance the ink-fiber detachment. It is clear from the above discussion that more work is needed in order to obtain a full understanding of the role of TX-100 in the pulping process.

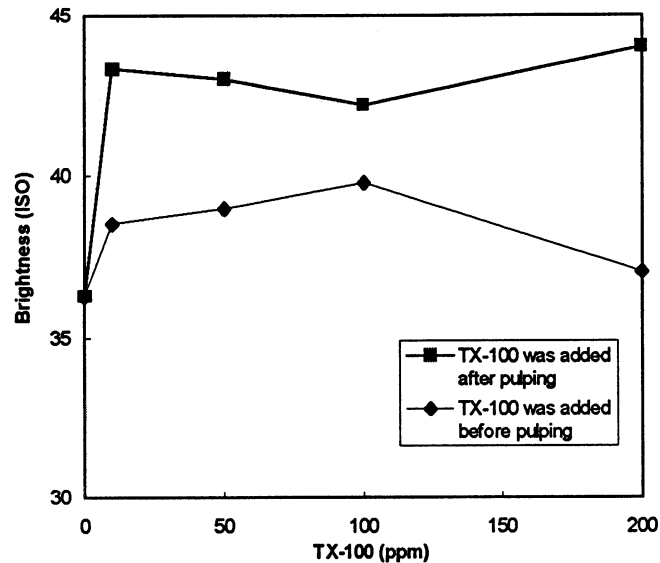


Fig. 17. Brightness of handsheet made by flotation deinked ONP (*Atlanta Journal-Constitution*) as a function of TX-100 concentration. ONP consistence during pulping: 1.31%; Pulp consistency in flotation cell: 0.5%; pH: 6.5; Nitrogen flow rate: 2000 cm³/min; flotation cell: column flotation cell with a 10 µm-air inlet filter.

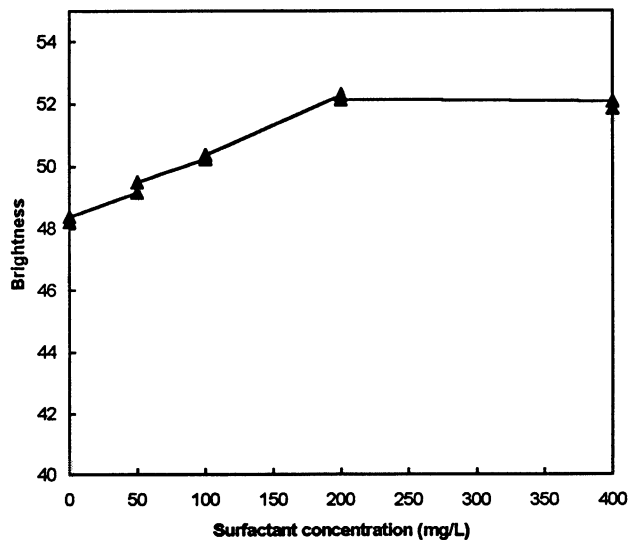


Fig. 18. Brightness of handsheet made from washed ONP. Surfactant was added in pulper. ONP consistency during pulping: 1.31%.

4. EFFECT OF OMG ON THE FLOTATION DEINKING OF ONP

4.1 Background

The deinking mills usually add certain amounts of OMG (10-30 %) to ONP in flotation deinking because the brightness of final products made from recycled fibers will increase in the presence of OMG. Because of the increase in OMG pricing, the paper recycling industry would like to reduce its consumption of OMG. Therefore, it is important to know what is the role of OMG in the flotation deinking of ONP.

Some authors [30-34] postulated that OMG can enhance ink removal from ONP pulp by some unknown reasons, but others [35-36] indicated that the addition of OMG will give no positive effect on ink removal during flotation.

Two reasons may be possible for the increase in the brightness of recycled ONP by adding OMG in flotation deinking:

- a) Addition of OMG will introduce fillers and high quality fibers into ONP resulting in an increase in the brightness, but will not enhance ink removal;
- b) There are some interactions among OMG, ONP, and process chemicals resulting an increase in ink removal efficiency.

In order to understand which mechanism is the dominating factor for the brightness increase in recycled ONP pulp after flotation, ONP handsheets were made by adding different ratios of OMG into ONP either before or after flotation deinking, and the brightness of these handsheets was examined in this study.

4.2. Experimental

ONP and OMG were separately pulped in the absence of surfactant. After pulping, the ONP and OMG were mixed under different ratios. After adding the required surfactant, the mixed pulps were subjected to flotation deinking using a

column flotation deinking cell. The brightness of the handsheet was measured using the method described in Section 3.2.

4.3. Results and Discussions

Fig. 19 shows the brightness of flotation deinked ONP handsheets as a function of calcium ion concentration after flotation in the presence of 100 ppm sodium oleic acid. It can be seen that, for 100% ONP, the brightness slightly increased with the increase in calcium concentration. This is consistent with previous reported results, i.e., water hardness will improve ink removal if fatty acid is used as a deinking chemical. However, there is almost no effect of calcium concentration on the handsheet brightness of OMG. This is not surprising because the calcium concentration in OMG pulps is already high enough due to dissolved calcium-containing fillers.

It also can be seen from Fig. 19 that the brightness of handsheets made of 70% ONP/30% OMG is a little higher than that of 100% ONP, but is consistently lower than that of 100% OMG. In order to know if this small brightness gain is due to the improvement of ONP deinking by adding OMG, two different experiments were conducted. In the first experiment, the ONP and OMG were separately pulped. After pulping, the 70% ONP was mixed with 30% OMG. The mixed pulp was deinked using the flotation technique. In the second experiment, the ONP and OMG were separately pulped and separately flotation deinked. After flotation deinking, these separately deinked pulps were mixed. The brightness of these two types of handsheets as a function of concentration of calcium ions is shown in Fig. 20. The assumption is that if OMG can really enhance the ink removal of ONP, the brightness of the handsheet should be higher when ONP and OMG are mixed before flotation. It can be clearly seen from Fig. 20 that the brightness of handsheets is lower if the OMG and ONP are mixed before flotation (<1 ISO). This result strongly suggests that the increase in brightness is solely due to the increase of the content of filler and high-quality pulp rather than the improvement of flotation deinking when OMG is mixed with ONP.

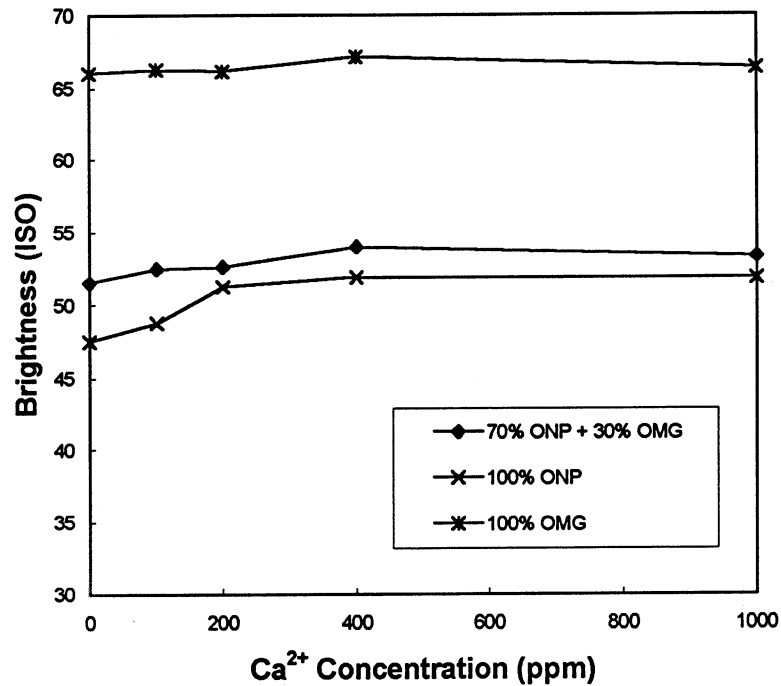


Fig. 19. The handsheet brightness of 100% ONP, 100% OMG, and the mixture of 70% ONP + 30% OMG as a function of Ca^{2+} concentration after flotation (ONP and OMG were mixed before flotation). Sodium oleic acid concentration: 100 mg/L; Fiber consistency: 0.5%; pH: neutral; Nitrogen flow rate: 18 cm³/min. The brightness was measured from the top side of the handsheet. No retention aid was used for handsheet making.

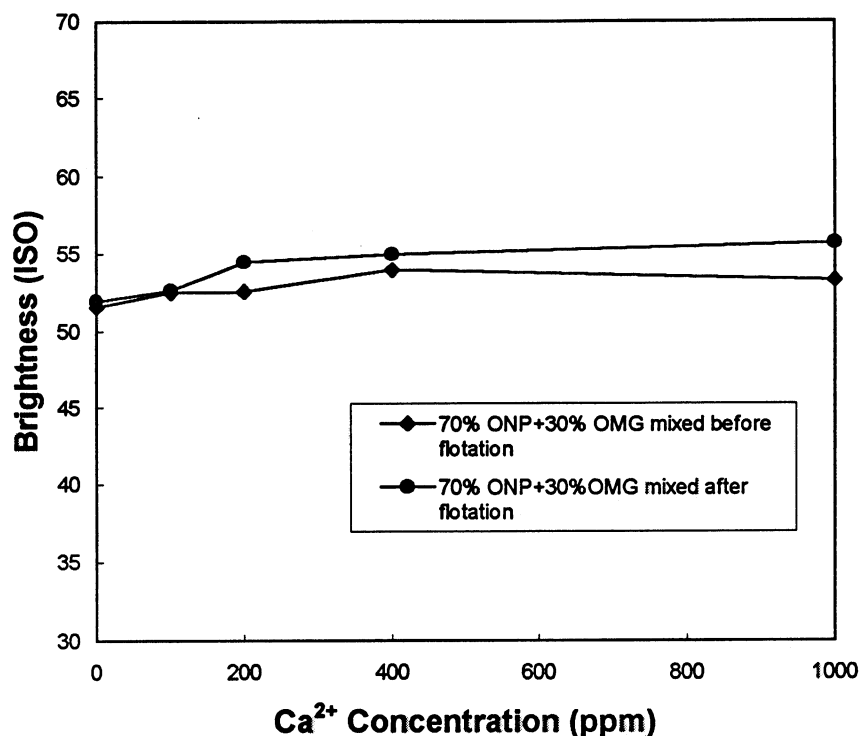


Fig. 20: The brightness of handseets made of 70% ONP plus 30% OMG as a function of calcium ion concentration. Sodium oleic acid concentration: 100 mg/L; Fiber consistency: 0.5%; pH: neutral; Nitrogen flow rate: 18 cm³/min. The brightness was measured from the top side of the handsheet. No retention aid was used for handsheet making.

The effect of OMG on ONP deinking was further studied by the flotation deinking of ONP in the presence of OMG filtrate or OMG fines. The OMG filtrate was obtained by filtering a 1.0% pulp slurry using a filter paper, and the OMG fines were obtained from the same pulp using a dynamic drainage jar (125 mesh). OMG fines of 453ml were mixed with the required ONP pulp (1.0%) to give 0.5% of total solid content. The mixed pulp slurry was subjected to flotation deinking in the presence of sodium oleic acid and calcium chloride. It is believed that if the brightness of ONP is improved by adding OMG filtrate after flotation deinking, the soluble polymers in the OMG filtrate will contribute to the ink removal of ONP. On the other hand, if the brightness of ONP will be improved by adding OMG fines after flotation deinking, the fines (mainly the fillers) in the OMG filtrate will be the major contributor to the ink removal. The results shown in

Fig. 21 are surprising because both the filtrate and the fines consistently reduced rather from increased the brightness of ONP. This observation supports the results obtained in Fig. 20, i.e., the addition of OMG in ONP will not give any positive effect on ink removal during flotation when sodium oleic acid/calcium chloride are used as deinking chemicals.

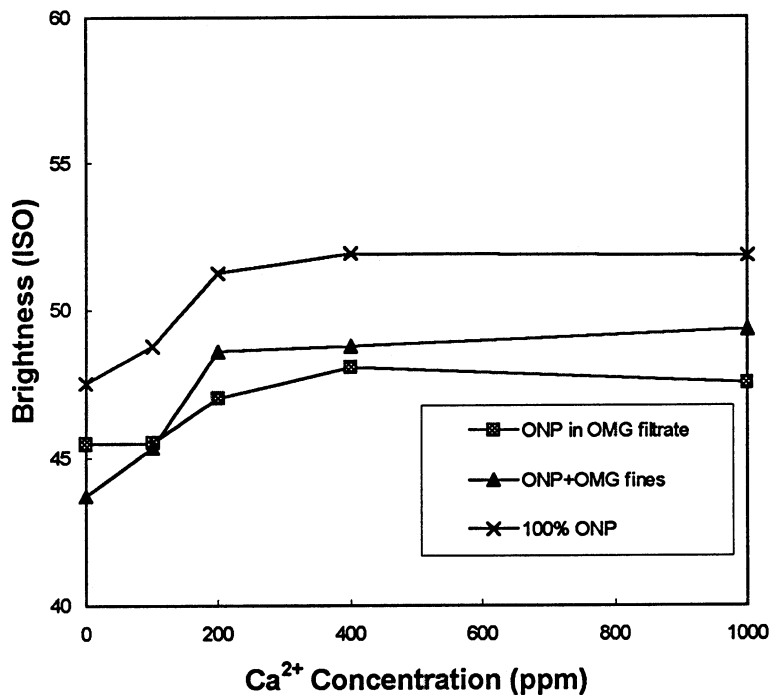


Fig. 20: The brightness of handseets made of ONP in the presence of OMG filtrate and OMG fines as a function of calcium ion concentration. Sodium oleic acid concentration: 100 mg/L; Fiber consistency: 0.5%; pH: neutral; Nitrogen flow rate: 2000 cm³/min. The brightness was measured from the top side of the handsheet. No retention aid was used for handsheet making.

4.4. Concluding Remarks

1. The increase of ONP brightness by adding OMG is not caused by improvement of ONP deinking efficiency, but is solely due to the increase of filler and high-quality fiber in recycled ONP.
2. Neither the soluble chemicals nor the fillers in OMG will improve the flotation deinking efficiency of ONP.

OBJECTIVES OF FY 98-99

1. Examine the filler chemistry (PCC and clay) in surfactant solutions (TX-100, oleic acid-calcium chloride, and cationic surfactants).
2. Study the filler flotation (PCC and clay) during flotation deinking.
3. Study the flotation deinking of ONP using cationic surfactants.
4. Investigate the effect of the remaining surfactant on the fiber surface chemistry and paper properties.

GOALS FOR FY 98-99

1. Fundamental understanding of filler flotation in deinking process.
2. Fundamental understanding of the effect of remaining surfactant on the fiber properties.
3. Evaluation of the advantages and disadvantages of using cationic surfactant in the flotation deinking.

DELIVERABLES

Four papers, "Contact angle measurement of wood fibers in surfactant and polymer solutions", "Effect of fiber surface chemistry on the fiber loss in flotation deinking", "Flotation deinking chemistry: the current research program at IPST", and "Collector chemistry in flotation deinking of xerographic papers" will be submitted to the scientific journals for the consideration of publication in FY99.

SCHEDULE IN MONTH

Tasks	1	2	3	4	5	6	7	8	9	10	11	12
1. Examine the filler chemistry (PCC and clay) in surfactant solutions (TX-100, oleic acid-calcium chloride, and cationic surfactants)	X	X	X									
2. Study the filler flotation (PCC and clay) in during flotation deinking			X	X	X	X						
3. Study the flotation deinking of ONP using cationic surfactants					X	X	X	X				
4. Investigate the effect of the remaining surfactant on the fiber surface chemistry and paper properties									X	X	X	X

REFERENCES

1. Ferguson, L. D. Deinking Chemistry: Part 1, Tappi J. **75** (7), 75 (1992).
2. Ferguson, L. D. Deinking Chemistry: Part 2, Tappi J. **75** (8), 49 (1992).
3. Amand, F. J. S. Hydrodynamics of Flotation: Experimental Studies and Theoretical Analysis. TAPPI Recycling Symp., TAPPI Press, Atlanta, GA, 219 (1997).
4. Dorris, G. M.; Page, M. Deinking of Toner-Printed Papers. Part 1: Flotation Kinetics, Froth Stability and Fiber Entrainment. J. Pulp Paper Sci., **23** (5), 206 (1997).
5. Dorris, G. M.; Sayegh, N. N. The Role of Print Layer Thickness and Cohesiveness on Deinking of Toner-printed Papers. Tappi J. **80** (4), 80 (1997).
6. Johnson, D. A.; Thompson, E. V. Fiber/toner Detachment Studies: Repulping and Flotation of Laser Printed Paper. Part I., Proc. TAPPI Pulping Conf., TAPPI Press, Atlanta, GA, 1291 (1995).
7. Snyder, B. A.; Berg, J. C. Liquid Bridge Agglomeration: A Fundamental Approach to Toner Deinking. TAPPI Recycling Symp., TAPPI Press, Atlanta, GA, 277 (1994).
8. Paulsen, F. G.; Berg, S. R.; Vidotti, R. M.; Johnson, D. A.; Thompson, E. V. Measurement of Long-Range Hydrophobic Attraction Forces and Their Relationship to Deinking Flotation. Part 2. TAPPI Recycling Symp., TAPPI Press, Atlanta, GA, 41 (1997).
9. Mak, N.; Stevens, J. Characteristics of Fatty Acid as an Effective Flotation Deinking Collector. 2nd Research Forum on Recycling (1993).
10. Johanson, B.; Wickman, M.; Strom, G. Mechanism of Offset Ink Particles Agglomeration in a Calcium-fatty Acid Collector System, J. Pulp Paper Sci., **22** (10), 381 (1996).
11. Epple, M.; Schmidt, D. C.; Berg, J. C. The Effect of Froth Stability and Wettability on the Flotation of a Xerographic Toner. Colloid & Polymer Sci., **272**, 1264 (1994).
12. Wasmund, B.; Pelton, R. Model Deinking Studies: Carbon Black Removal by Oil-Coated Beads. Pulp Conference Proc., TAPPI Press, Atlanta, GA, 1005 (1994).
13. Miller, J. D.; Azevedo, M. A. D.; Xie, X.; Drelich J. Recycling Office Waste - Recovered Paper Deinking Research at the University of Utah, In Paper

- Recycling Challenge Vol. 2 - Deinking & Bleaching, Doshi, M. R. and Dyer, J. M. Eds., Doshi & Associates Inc., Appleton, WI, 167, (1997).
14. Oguz, M.; Enuysal, M. Recovery of Deinked Paper Stock from Waste Newspapers. *International J. Environmental Studies A & B*, 263 (1994).
 15. Shergold, H. L. Cationic Surfactants in Mineral Processing. *Industrial Application of Surfactants, the Proceedings of a Symposium Organized by the North West Region of the Industrial Division of Royal Society of Chemistry, University of Salford*, 269 (1986).
 16. James, A. D.; Ogden, P. H.; Wates, J. M. Cationic Surfactants. *Industrial Application of Surfactants, the Proceedings of a Symposium Organized by the North West Region of the Industrial Division of Royal Society of Chemistry, University of Salford*, 251 (1986).
 17. Kenny, F. J. Use of Surfactant in Mineral Flotation. *Industrial Application of Surfactants II, The Proceedings of a Symposium Organized by the North West Region of the Industrial Division of Royal Society of Chemistry*, 367, University of Salford, (1989).
 18. Borchardt, J. K. An Introduction to Deinking Chemistry. In *Paper Recycling Challenge Vol. 2: Deinking & Bleaching*, Doshi, M. R. and Dyer, J. M. Eds., Doshi & Associates Inc., WI, Appleton, (1997).
 19. Putz, H. J.; Schaffrath, H. J.; Gottsching, L. Deinking of Oil- and Water-Borne Printing Inks: A New Flotation Deinking Model, *Pulp and Paper Canada*, **94 (7)** 193, (1993).
 20. Turvey, R. W. Why Do Fibers Float, *J. Pulp Paper Sci.*, **19**, 52 (1993).
 21. Turvey, R. W. Stock Loss as a Function of Water Hardness in Flotation Deinking, *Paper Techn. Ind.*, 366 (1987).
 22. Li, M.; Muvundamina, M. Fractionation of Fiber Slurries via Froth Flotation and Sedimentation, *Prog. Pap. Recycling*, **4 (3)**, 32 (1995).
 23. Deng, Y.; Abazeri, M. True Flotation and Physical Entrainment: The Mechanisms of Fiber Loss in Flotation Deinking, *Nordic Pulp Paper Res. J.*, in press.
 24. Ajersch, M.; Pelton, R. Mechanisms of Pulp Loss in Flotation Deinking, *J. Pulp Paper Sci.*, **22 (9)**, 338 (1996).
 25. Deng, Y. Fundamentals of Surface Chemistry in Flotation Deinking, *IPST Annual Report*, (1997).

26. Warren, L. Determination of the Contributions of True Flotation and Entrainment in Batch Flotation Tests, *Int. J. Min. Proc.* **14**, 34 (1985).
27. Ishibashi, Y.; Myauchi, Y.; Inoe, M. Japanese Patent 06 49 790, February 24 (1994).
28. Masamizu, K.; Tai, Y.; Hagiwara, M.; Ukigai, T. Development of Deinking Agents for Flotation Systems, *Proc. TAPPI Pulping Conf.*, 39, TAPPI Press, Atlanta, GA, (1994).
29. Borchardt, J. An introduction to Deinking Chemistry, in *Paper Recycling Challenge Vol. 2: Deinking & Bleaching*, Eds. Doshi, M. R. and Dyer, J. M., Doshi & Associates Inc., Appleton WI, 18, (1997).
30. Morel, P. Secondary Fiber for Newsprint. *TAPPI Pulping Conf.*, TAPPI Press, Atlanta, GA, 367 (1989).
31. Fulton, T. Improved Deinked Pulp for Newsprint, *Pulping Conf.*, TAPPI Press, Atlanta, GA, 535 (1997).
32. Rao, R.; Kuys, K.; Abbot, J. The Role of Coated Paper and Fillers in Flotation Deinking of Newsprint, *Progress in Paper Recycling*, **5** (2), 103, (1996).
33. Schriver, K.; Bingham, S.; Fraizer, M. The Function of Clay in Flotation Deinking, *Pulping Conference*, 133 (1990).
34. Schriver, K. Mill Chemistry Must Be Considered Before Making Deink Line Decision, *Pulp & Paper*, **64** (3), 76 (1990).
35. Mahagaonkar, M; Stack, K.; Banham, P. The Effects of Coated Magazines on Deinking of Newsprint After Pulping and Flotation, *Recycling Symposium*, TAPPI Press, Atlanta, GA, 193 (1997).
36. Letscher, M.; Sutman, F. The Effect of Magazine and Filler on the Flotation Deinking of Newsprint, *J. Pulp and Paper Sci.*, **28** (6), 225 (1992).

